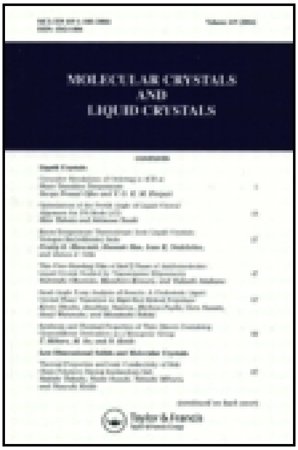

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# Kinetics of the Phase Transition of Poly(p-Biphenylyl Acrylate)

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# KINETICS OF THE PHASE TRANSITION OF POLY(p-BIPHENYLYL ACRYLATE)

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Abstract The kinetics of the isotropic-to-smectic A transition of poly(p-biphenylyl acrylate) has been investigated by differential scanning calorimetry. The parameter n of the Avrami equation has been found to be of ca. 3. The calculated formation energy of the nuclei is $40\div50$ KJ·mole$^{-1}$. From the thermal data, it is concluded that, in this polymer, a fraction of amorphous material is present together with the mesophase, and the relative amounts of the two phases varies with the thermal history.

## INTRODUCTION

The kinetics of the phase transitions of a number of low molecular mass liquid crystals have been studied about ten years ago by Price and Wendorff[1]. The transitions in these systems are characterized by very small degree of undercooling (about 0.1 deg) and by very high rate of transformation (even at this small undercooling). To our knowledge, no kinetic study has been published so far concerning the phase transitions occurring in liquid crystalline side-chain polymers.

Poly(p-biphenylyl acrylate)[†] (PPBA) is a thermotropic polymer characterized by a smectic A phase, the range of stability of which extends up to about 540 K[2]. At low temperatures (below the glass transition temperature $T_g \simeq 380$ K) the polymer is frozen in as a mesomorphic glass, whereas, at temperatures between $T_g$ and $T_i$, it behaves as a semisolid material.

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[†] Systematic name: Poly(4-biphenylyloxycarbonylethylene)

The first-order smectic-to-isotropic transition is accompanied by an appreciable heat absorption (ca. 20 $J \cdot g^{-1}$)[3]. The formation of the mesophase from the isotropic melt takes place exothermally with a relatively high undercooling. In fact, as it is shown in Fig. 1, the exotherm on the cooling DSC trace is observed at a temperature $T_s$ which is about 20 K lower than $T_i$ (for a cooling rate of 30 $K \cdot min^{-1}$); however, the isotropic melt can be even quenched in ice-water to give a fully amorphous, transparent glass[4].

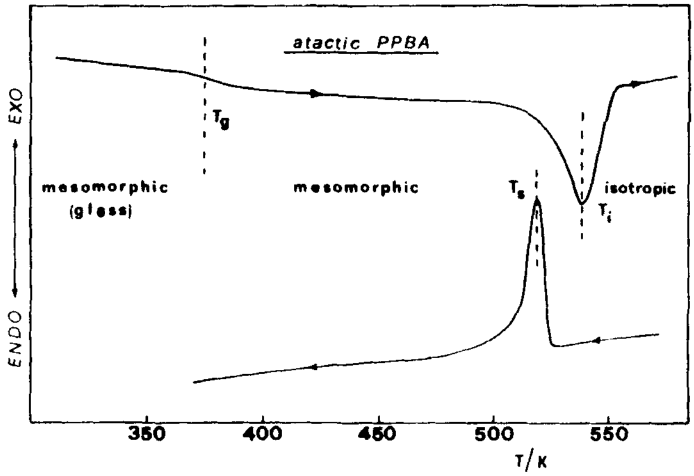

FIGURE 1 DSC heating and cooling traces of atactic PPBA.

Since PPBA can be easily cooled below $T_i$ without appreciable transformation of the isotropic phase, the kinetics of the isothermal mesophase formation, at different $T_s$ values, can be conveniently investigated.

In this paper we present the results of a kinetic study of the formation of the smectic phase from the isotropic melt of PPBA, carried out by differential scanning calorimetry.

## EXPERIMENTAL

PPBA was prepared by bulk polymerization of the corresponding monomer, initiated by $Bz_2O_2$ at 60 C, as described previously.[5] The crude polymer was fractionated with boiling benzene and the insoluble fraction was dissolved in $CHCl_3$, precipitated in excess methanol and dried. The polymer had $\overline{M}n = 91.2 \cdot 10^3$ and $\overline{M}w/\overline{M}n = 4.9$.[3]

The kinetic measurements were made on a differential scanning calorimeter, Perkin Elmer DSC-2, by first heating the polymer samples (7÷9 mg) to 590 K for 5 min, in order to cancel any effect of previous thermal history, and cooling them rapidly (in the instrument) down to the selected transformation temperature $T_S$: the heat evolved during the isothermal formation of the mesophase was then recorded as a function of time[6]. After the completion of the transformation, as revealed by the DSC trace, the temperature was again raised at a rate of 10 $K{\cdot}min^{-1}$ in order to register the endotherm of isotropization of the mesophase formed.

The same sample could be used for successive runs carried out at different $T_S$, since no appreciable sign of polymer decomposition was observed. The reproducibility of the results was very satisfactory either on rerunning the same sample or by using new ones.

## RESULTS AND DISCUSSION

An example of the DSC trace registered during the isothermal mesophase formation in a PPBA sample cooled rapidly from 590 K to the temperature $T_S$ is shown in Fig. 2. From the trace, the fraction $X_t$ of the polymer transformed at the time t can be determined as the ratio of the area of the exotherm, at the time t, to that of the overall exotherm.

The range of transformation temperatures investigated is between 526 and 534 K. For higher temperatures, the transformation was too slow to allow an accurate measurement of the kinetic parameters; for lower temperatures, the transformation started before the end of the cooling down to $T_S$. An induction period was observed at all temperatures, except the two lowest investigated.

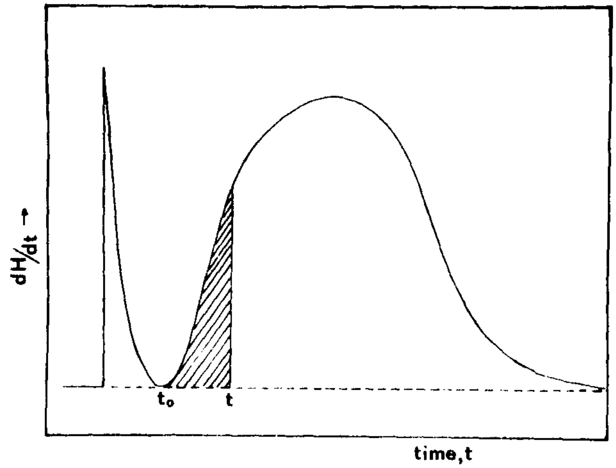

FIGURE 2 DSC trace registered isothermally at $T_s$.

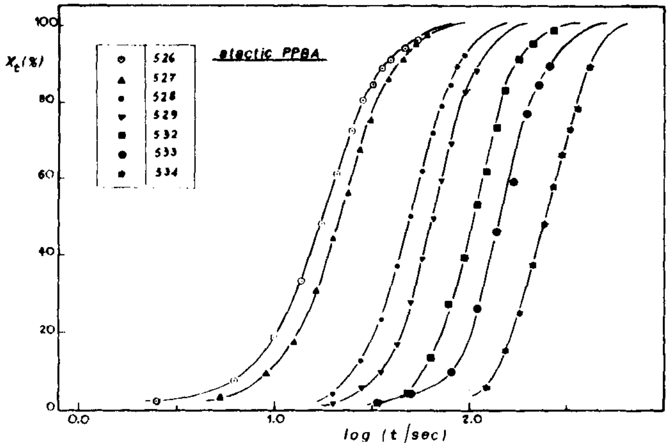

FIGURE 3 Isotherms of the mesophase formation of PPBA.

The values of $X_t$ are plotted as a function of time, for some of the temperatures $T_s$ investigated, in Fig. 3. All the curves have the same shape and are superimposable on each other by an appropriate shift along the time axis. This indicates that the transition investigated may be analyzed in terms of the Avrami[7] equation:

$$1 - X_t = \exp(-K_n \cdot t^n) \quad (1)$$

where n depends on the modes of the nucleation and on the geometry of growth of the transforming regions and $K_n$ is a constant depending on nucleation density and on the growth of the transformation.

The plots of $\log\{-\ln(1-X_t)\}$ vs. $\log t$, at different values of $T_s$, are presented in Fig. 4. The experimental data may be described by straight lines, as required by equation (1), up to sufficiently high conversions (70÷80%). The kinetic parameters are collected in Table 1.

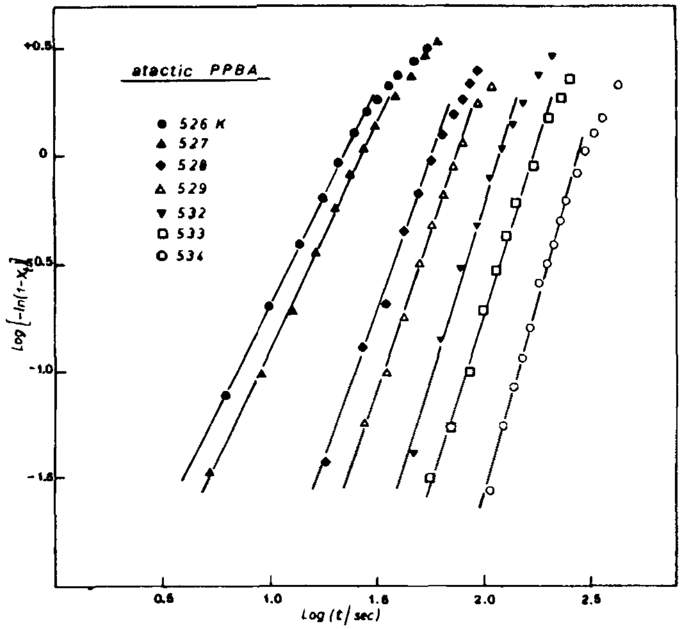

FIGURE 4 Avrami plots for the mesophase formation in PPBA samples at the temperatures $T_s$ indicated.

At $T_s$ lower than 528 K, the transformation was very fast and started before the rapid cooling of the sample down to

TABLE 1 Kinetic parameters of the phase transition of Poly(p-biphenylyl acrylate)

| $T_s$ (K) | $t_{0.5}$ (sec) | Avrami corr.coeff. | n | $K_n=\ln 2/t_{0.5}^3$ ($sec^{-3}$) | $T_i$ (K) | $\Delta H_i$ ($J\cdot g^{-1}$) |
|---|---|---|---|---|---|---|
| 526 | (18) | 0.999 | (2.0) | ($1.19\cdot10^{-4}$) | (545.4) | 12.5 |
| 527 | (22) | 0.999 | (2.1) | ($6.51\cdot10^{-5}$) | (542.5) | 13.0 |
| 528 | 50 | 0.994 | 2.8 | $5.54\cdot10^{-6}$ | 544.0 | 8.8 |
| 529 | 65 | 0.998 | 2.9 | $2.52\cdot10^{-6}$ | 544.2 | 8.4 |
| 530 | 72 | 0.995 | 2.8 | $1.86\cdot10^{-6}$ | 545.3 | 7.1 |
| 531 | 90 | 0.994 | 2.8 | $0.95\cdot10^{-6}$ | 545.5 | 7.9 |
| 532 | 105 | 0.996 | 3.2 | $5.99\cdot10^{-7}$ | 547.0 | 9.5 |
| 533 | 146 | 0.996 | 3.1 | $2.23\cdot10^{-7}$ | 547.0 | 7.1 |
| 534 | 248 | 0.998 | 3.6 | $4.54\cdot10^{-8}$ | 547.5 | 6.6 |

the selected $T_s$ was completed: as it is shown in Fig. 4 and in Table 1, for these runs, the slope of the straight lines corresponds to ca. $n = 2$. This same value was found by Price and Wendorff[1] for the isotropic-to-mesomorphic transition of most of the low molecular mass liquid crystals investigated by them.

For all other $T_s$ values investigated, the complete exotherm of transformation could be registered and the straight lines slopes correspond to an average value $\bar{n} = 3.0 \pm 0.3$, which can be interpreted in terms of both athermal and thermal nucleation, followed by three-dimensional growth.

For higher conversions, n decreases down to ca. 1, thus indicating that secondary processes become operative which lead to an increase of the amount of the mesomorphic phase.

The values of the half-times of transformation are shown in Table 1 and in Fig. 5. For comparable degrees of undercooling, the half-times appear much lower than those obtained for the isothermal crystallization of high polymers such as isotactic polystyrene[8]. However, from a kinetic point of view, the isotropic-to-smectic transition examined here can be considered similar to the crystallization of polymers and, therefore, analyzed in terms of the kinetic theory of the crystallization of polymers[9]. The dependence of the transition rate, here expressed as $1/t_{0.5}$, on the temperature $T_s$ can be corre-

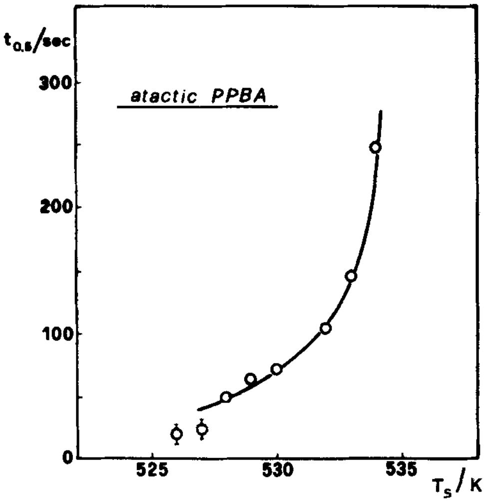

FIGURE 5 Half-times of transformation vs. $T_s$

lated with the energy of formation of nuclei of critical dimensions, for undercooling values $\Delta T = T_i^o - T_s$ (where $T_i^o$ = = 571 K is the equilibrium temperature of isotropization, calculated as described below), through the equation (derived from the Turnbull-Fischer equation):

$$\log(1/t_{0.5}) = A_s - \frac{B_s}{2.3 \cdot K} \cdot \frac{T_i^o}{T_s \cdot \Delta T} \qquad (2)$$

where $B_s \cdot T_i^o/\Delta T$ is the energy of formation of the nuclei and $B_s$ is a term which accounts for the interfacial energy of the growing surfaces, the dimensions of the nuclei and the enthalpy of transition per unit volume; $A_s$ depends on the density of nucleation and on the energy of transport of the molecules and can be considered constant, at first approximation, in the temperature range investigated.

As required by equation (2), the plot of $\log(1/t_{0.5})$ vs. $T_i^o/T_s\Delta T$ is in fact linear, as it is demonstrated by the graph in Fig. 6. From the slope of the straight line, the values of the formation energy of the nuclei have been found to vary between 42 and 50 KJ/mol for $T_s$ in the range 526÷534 K. It is noteworthy that these values are close to those found for the crystallization of e.g. isotactic polystyrene, for comparable degrees of undercooling[8].

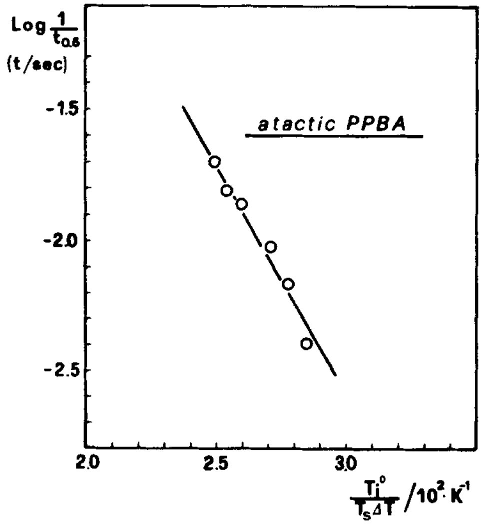

FIGURE 6 Plot of equation (2)

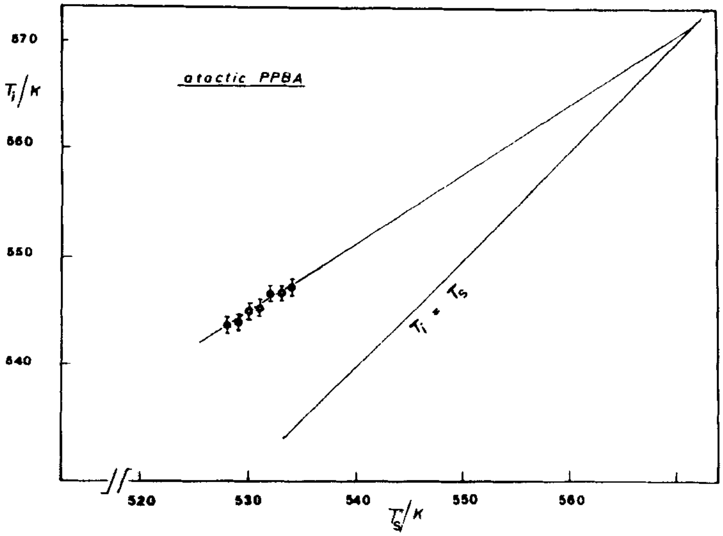

FIGURE 7 Isotropization temperatures $T_i$ of samples of PPBA isothermally transformed at $T_s$

The value of $T_i^o$ has been calculated by extrapolation of the values of the isotropization temperatures $T_i$ of the mesophases formed at different $T_s$ (Fig. 7). This value is higher than that previously calculated for an atactic PPBA sample with 35% syndiotacticity (550 K), and slightly lower than that found for a sample with 65% syndiotacticity (578 K)[10]. A different content of syndiotacticity of the sample investigated here, as well as the difference in the experimental techniques may be responsible for the different values obtained.

The plot of Fig. 7 demonstrates that the isotropization temperature increases with increasing the temperature at which the mesophase has been formed, thus showing that the domains formed at higher temperatures are larger and/or better ordered than those formed at lower temperatures.

On the contrary, the data of Table 1 indicate that, the lower the temperature $T_s$, the higher is the isotropization enthalpy: this demonstrates that the fraction of polymer which can be transformed into the mesophase decreases with increasing the transformation temperature. On the other hand, if the sample is cooled to room temperature after the isothermal transformation is over, a well resolved two-peak pattern is observed in the subsequent DSC trace: the higher temperature peak corresponds to the isotropization of the mesophase formed isothermally at $T_s$, and the lower temperature one to that formed during the cooling step.

These conclusions agree with the diffractometric data obtained recently[11] for the same polymer at different temperatures: in fact, the intensity of the low angle reflection associated with the spacing of the smectic layers, which is a measure of the degree of mesomorphism of the sample, decreases steadily to very low values on increasing the temperature in an interval containing the range investigated here.

All these facts demonstrate that PPBA can certainly be obtained as a two-phase material, composed by a smectic phase plus an amorphous phase. The amount of either phase can be varied to a large extent by changing the conditions for the mesophase formation. Almost no mesophase is formed if the isotropic melt is quenched in ice-water. But a fraction of amorphous glass is certainly present also in the slowly cooled polymer samples and is probably responsible for the glass transition observed in the DSC traces of PPBA at ca. 380 K (cf. Fig. 1).

A different conclusion was reached by Frenzel and Rehage[12] through PVT measurements made on liquid crystalline polymers containing flexible spacers between the main chains and the mesogenic side-groups. In fact, these polymers were shown to behave as thermodynamically homogeneous materials, like low molecular mass liquid crystals. This different behaviour can perhaps be explained easily considering the basically different flexibility of the two types of macromolecular compounds.

Our conclusion is also at variance with that drawn by Menczel and Wunderlich[13] from a calorimetric study of poly-(p-acryloyloxybenzoic acid), and no simple explanation can be offered to account for this discrepancy.

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